

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference EL00014PCT	FOR FURTHER ACTION see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. PCT/JP 00/ 05858	International filing date (day/month/year) 30/08/2000	(Earliest) Priority Date (day/month/year) 31/08/1999
Applicant TOKYO ELECTRON LIMITED et al.		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.
☒ It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.

☐ as suggested by the applicant.

☒ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

1
☐ None of the figures.

INTERNATIONAL SEARCH REPORT

International Application No

PC 00/05858

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C23C16/455

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 821 084 A (APPLIED MATERIALS INC) 28 January 1998 (1998-01-28) column 8, line 22 -column 9, line 1 ---	1-14
A	PATENT ABSTRACTS OF JAPAN vol. 017, no. 538 (E-1440), 28 September 1993 (1993-09-28) & JP 05 152208 A (FUJITSU LTD), 18 June 1993 (1993-06-18) abstract ---	1-14
A	PATENT ABSTRACTS OF JAPAN vol. 010, no. 141 (E-406), 24 May 1986 (1986-05-24) & JP 61 005515 A (FUJITSU KK), 11 January 1986 (1986-01-11) abstract --- -/--	1-14



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- * & * document member of the same patent family

Date of the actual completion of the international search

28 November 2000

Date of mailing of the international search report

04/12/2000

Name and mailing address of the ISA

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Authorized officer

Ekhult, H

INTERNATIONAL SEARCH REPORT

International Application No

PC 00/05858

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category.	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	<p>US 5 976 261 A (MOSLEHI MEHRDAD M ET AL) 2 November 1999 (1999-11-02) column 7, line 1 - line 23 -----</p>	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/JP 00/05858

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0821084 A	28-01-1998	US 6090210 A JP 10121253 A	18-07-2000 12-05-1998
JP 05152208 A	18-06-1993	NONE	
JP 61005515 A	11-01-1986	NONE	
US 5976261 A	02-11-1999	NONE	

PCT REQUEST

Original (for SUBMISSION) - printed on 29.08.2000 11:00:47 AM

0	For receiving Office use only	
0-1	International Application No.	
0-2	International Filing Date	
0-3	Name of receiving Office and "PCT International Application"	
0-4	Form - PCT/RO/101 PCT Request Prepared using	PCT-EASY Version 2.91 (updated 01.07.2000)
0-5	Petition The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty	
0-6	Receiving Office (specified by the applicant)	Japanese Patent Office (RO/JP)
0-7	Applicant's or agent's file reference	EL00014PCT
I	Title of invention	FILM DEPOSITION APPARATUS AND METHOD
II	Applicant	
II-1	This person is:	applicant only
II-2	Applicant for	all designated States except US
II-4	Name	TOKYO ELECTRON LIMITED
II-5	Address:	3-6, Akasaka 5-Chome, Minato-Ku, Tokyo 107-8481 Japan
II-6	State of nationality	JP
II-7	State of residence	JP
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III-1-6	State of nationality	JP
III-1-7	State of residence	JP

PCT REQUEST

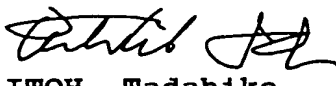
Original (for SUBMISSION) - printed on 29.08.2000 11:00:47 AM

III-2	Applicant and/or inventor	
III-2-1	This person is:	applicant and inventor
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III-2-6	State of nationality	JP
III-2-7	State of residence	JP
IV-1	Agent or common representative; or address for correspondence	
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IV-1-1	Name (LAST, First)	ITOH, Tadahiko
IV-1-2	Address:	32nd Floor, Yebisu Garden Place Tower, 20-3, Ebisu 4-chome, Shibuya-ku, Tokyo 150-6032 Japan
IV-1-3	Telephone No.	03-5424-2511
IV-1-4	Facsimile No.	03-5424-2525
V	Designation of States	
V-1	Regional Patent (other kinds of protection or treatment, if any, are specified between parentheses after the designation(s) concerned)	EP: AT BE CH&LI CY DE DK ES FI FR GB GR IE IT LU MC NL PT SE and any other State which is a Contracting State of the European Patent Convention and of the PCT
V-2	National Patent (other kinds of protection or treatment, if any, are specified between parentheses after the designation(s) concerned)	KR US
V-5	Precautionary Designation Statement In addition to the designations made under items V-1, V-2 and V-3, the applicant also makes under Rule 4.9(b) all designations which would be permitted under the PCT except any designation(s) of the State(s) indicated under item V-6 below. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit.	
V-6	Exclusion(s) from precautionary designations	NONE

PCT REQUEST

EL00014PCT

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VI-1	Priority claim of earlier national application		
VI-1-1	Filing date	31 August 1999 (31.08.1999)	
VI-1-2	Number	Patent Application 11-245836	
VI-1-3	Country	JP	
VII-1	International Searching Authority Chosen	European Patent Office (EPO) (ISA/EP)	
VIII	Check list	number of sheets	electronic file(s) attached
VIII-1	Request	4	-
VIII-2	Description	29	-
VIII-3	Claims	6	-
VIII-4	Abstract	1	e100014.txt
VIII-5	Drawings	8	-
VIII-7	TOTAL	48	
	Accompanying items	paper document(s) attached	electronic file(s) attached
VIII-8	Fee calculation sheet	✓	-
VIII-9	Separate signed power of attorney	✓	-
VIII-10	Copy of general power of attorney	✓	-
VIII-12	Priority document(s)	Item(s) VI-1	-
VIII-16	PCT-EASY diskette	-	diskette
VIII-17	Other (specified):	Revenue stamps of transmittal fee for receiving office	-
VIII-17	Other (specified):	Submission of certificate of payment for search fee	-
VIII-17	Other (specified):	Submission of certificate of payment for international fee	-
VIII-18	Figure of the drawings which should accompany the abstract		
VIII-19	Language of filing of the international application	English	
IX-1	Signature of applicant or agent		
IX-1-1	Name (LAST, First)	ITOH, Tadahiko	

FOR RECEIVING OFFICE USE ONLY

10-1	Date of actual receipt of the purported international application	
10-2	Drawings:	
10-2-1	Received	
10-2-2	Not received	
10-3	Corrected date of actual receipt due to later but timely received paper drawings completing the purported international application	

PCT REQUEST

EL00014PCT

Original (for SUBMISSION) - printed on 29.08.2000 11:00:47 AM

10-4	Date of timely receipt of the required corrected drawings under PCT Article 11(2)	
10-5	International Searching Authority	ISA/EP
10-6	Transmittal of search copy delayed until search fee is paid	

FOR INTERNATIONAL BUREAU USE ONLY

11-1	Date of receipt of the record copy by the International Bureau	
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PARENT COOPERATION TREATY

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From the INTERNATIONAL BUREAU

NOTIFICATION CONCERNING
SUBMISSION OR TRANSMITTAL
OF PRIORITY DOCUMENT

(PCT Administrative Instructions, Section 411)

To:

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JAPON

Date of mailing (day/month/year) 22 September 2000 (22.09.00)	
Applicant's or agent's file reference EL00014PCT	IMPORTANT NOTIFICATION
International application No. PCT/JP00/05858	International filing date (day/month/year) 30 August 2000 (30.08.00)
International publication date (day/month/year) Not yet published	Priority date (day/month/year) 31 August 1999 (31.08.99)
Applicant TOKYO ELECTRON LIMITED et al	

1. The applicant is hereby notified of the date of receipt (except where the letters "NR" appear in the right-hand column) by the International Bureau of the priority document(s) relating to the earlier application(s) indicated below. Unless otherwise indicated by an asterisk appearing next to a date of receipt, or by the letters "NR", in the right-hand column, the priority document concerned was submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b).
2. This updates and replaces any previously issued notification concerning submission or transmittal of priority documents.
3. An asterisk(*) appearing next to a date of receipt, in the right-hand column, denotes a priority document submitted or transmitted to the International Bureau but not in compliance with Rule 17.1(a) or (b). In such a case, the attention of the applicant is directed to Rule 17.1(c) which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.
4. The letters "NR" appearing in the right-hand column denote a priority document which was not received by the International Bureau or which the applicant did not request the receiving Office to prepare and transmit to the International Bureau, as provided by Rule 17.1(a) or (b), respectively. In such a case, the attention of the applicant is directed to Rule 17.1(c) which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.

<u>Priority date</u>	<u>Priority application No.</u>	<u>Country or regional Office or PCT receiving Office</u>	<u>Date of receipt of priority document</u>
31 Augu 1999 (31.08.99)	11/245836	JP	18 Sept 2000 (18.09.00)

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(19) World Intellectual Property Organization
International Bureau



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11/245836 31 August 1999 (31.08.1999) JP

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Hosaka-cho, Nirasaki-shi, Yamanashi 407-0192 (JP). **MATSUMOTO, Kenji [JP/JP]**; Tokyo Electron Limited, 650, Mitsuzawa, Hosaka-cho, Nirasaki-shi, Yamanashi 407-0192 (JP).

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(81) Designated States (national): KR, US.

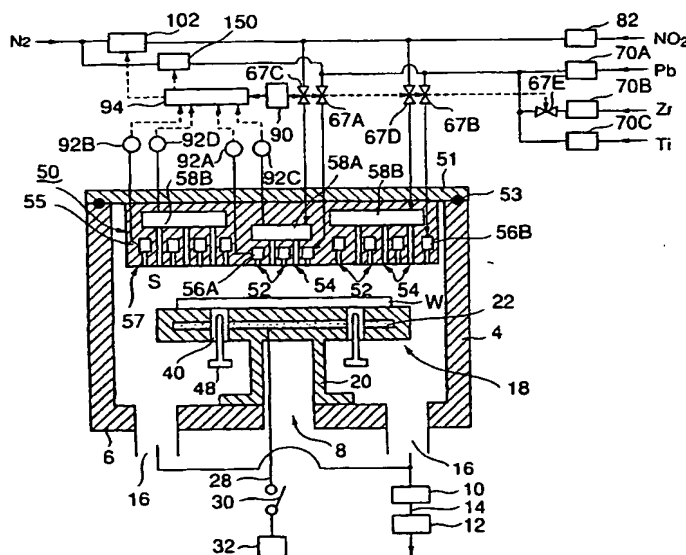
(84) Designated States (regional): European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published:

— With international search report.

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: **FILM DEPOSITION APPARATUS AND METHOD**



(57) Abstract: A film deposition apparatus (2) forms a PZT film at a high deposition rate under a low temperature by using a single showerhead (50) throughout the deposition process. Process gases including a raw material gas and an oxidant gas are introduced into a process chamber (4) in which a wafer (W) is accommodated. The process chamber (4) is maintained at a predetermined vacuum during the film depositing process. A gas injection surface (57) of the shower head (50) from which the process gases are injected is divided into an inner zone (84) covering a center portion of the wafer (W) and an outer zone (86) surrounding the inner zone (84). The raw material gas is separately injected from the inner zone (84) and the outer zone (86), and the oxidant gas is separately injected from the inner zone (84) and the outer zone (86).

WO 01/16396 A1

DESCRIPTION

FILM DEPOSITION APPARATUS AND METHOD

5 TECHNICAL FIELD

The present invention generally relates to a film deposition apparatus and method, and, more particularly, to a film deposition apparatus and method for depositing a PZT film on a semiconductor wafer.

10

BACKGROUND ART

A PZT film can be obtained as a crystal film of $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ having a perovskite structure by making an organometallic material gas react with an oxidant gas such as NO_2 gas in a chemical vapor deposition (CVD) process apparatus. The organometallic material gas contains $\text{Pb}(\text{DPM})_2$ (Bisdipivaloyl-methanatolead : $\text{Pb}(\text{C}_{11}\text{H}_{19}\text{O}_2)_2$), $\text{Zr}(\text{t-OC}_4\text{H}_9)_4$ (Tetratertiary-butoxyzirconium) and $\text{Ti}(\text{I-OC}_3\text{H}_7)_4$ (Tetraisopropoxy-titanium). Pb refers to lead, Zr refers to zirconium, and Ti refers to titanium. The PZT film has attracted great attention as a memory capacitor material of a second-generation planar stack type FeRAM.

Generally, in order to deposit an oxide film such as a PZT film in a crystal state, a wafer or substrate on which the oxide film is deposited must be heated to a temperature as high as about 600°C . However, in a case in which a structure having weakness against heat is previously formed on the wafer or substrate, the film deposition process must be performed by a two-stage process including a process of forming a crystalline nucleus and a process of growing the crystal so as to decrease the process temperature of the film deposition process. The degrees of vacuum appropriate for the two

processes are not always equal to each other. Thus, it is required to perform a low vacuum process and a high vacuum process by using a single chamber. However, since there is no showerhead, which can be used for both the high
5 vacuum process and the low vacuum process, the two-stage process must be performed by using two different chambers.

When an organometallic material (MO) is used in a gaseous state, the organometallic material gas must be heated due to its low vapor pressure. Accordingly, if the
10 organometallic material gas meets an oxidant gas within a supply pipe, the organometallic material gas immediately reacts with the oxidant gas within the supply pipe, which results in deposition or formation of particles within the supply pipe. In order to eliminate such a problem, when
15 the organometallic material gas is used, a post mix type showerhead is normally used so as to mix the organometallic material gas with the oxidant gas after exiting the showerhead. However, it is difficult to eliminate leakage between the organometallic material gas
20 and the oxidant gas in the showerhead due to the construction of the showerhead. That is, there is a small air gap formed between the passages of the organometallic material gas and the oxidant gas due to the fabrication method of the showerhead. Thus, a gas leakage occurs
25 between the areas of the organometallic material gas and the oxidant gas in the showerhead, which results in deposition of the oxidized organometallic material or generation of particles of the oxidized organometallic material.

30

DISCLOSURE OF INVENTION

It is a general object of the present invention to provide an improved and useful film deposition

apparatus and method in which the above-mentioned problems are eliminated.

A more specific object of the present invention is to provide a film deposition apparatus and method which
5 can form a PZT film at a high deposition rate under a low temperature by using a single showerhead throughout the deposition process.

In order to achieve the above-mentioned objects, there is provided according to one aspect of the present
10 invention a film deposition apparatus for depositing a film on an object to be processed, the film deposition apparatus comprising: a process chamber accommodating the object therein; process gas supplying means for supplying process gases including a raw material gas and an oxidant
15 gas; evacuating means for evacuating the process gases from the process chamber so as to maintain the process chamber to be at a predetermined vacuum; and process gas introducing means for introducing the process gases supplied from the process gas supplying means into the
20 process chamber, wherein the process gas introducing means is configured and arranged to inject the process gases to an entire surface of the object, a gas injection surface from which the process gases are injected being divided into an inner zone covering a center portion of the object
25 and an outer zone surrounding the inner zone; and the process gas supplying means selectively supplies the process gases to the process gas introducing means so that the raw material gas is separately injected from the inner zone and the outer zone, and the oxidant gas is separately
30 injected from the inner zone and the outer zone.

According to the above-mentioned invention, crystalline nucleuses can be efficiently formed on the object to be processed such as a wafer by injecting the

raw material gas to the center portion of wafer and the oxidant gas to the peripheral portion of the wafer surrounding the center portion while maintaining the process chamber at a high vacuum. After the crystalline nucleuses are formed on the wafer, the crystal of the film can be grown at a high rate by injecting the raw material gas and the oxidant gas uniformly to the entire surface of the wafer at a relatively low temperature while maintaining the process chamber at a relatively low vacuum.

10 In the film deposition apparatus according to the present invention, the process gas supplying means may include switching means for switching the supply of the raw material gas to the process gas introducing means so that the raw material gas is selectively injected from either the inner zone alone or both the inner zone and the outer zone and the oxidant gas is selectively injected from either the outer zone alone or both the inner zone and the outer zone.

20 In one embodiment of the present invention, the process gas supplying means may include a first raw material gas supply passage supplying the raw material gas to the inner zone, a second raw material gas supply passage supplying the raw material gas to the outer zone, a first oxidant gas supply passage supplying the oxidant gas to the inner zone and a second oxidant gas supply passage supplying the oxidant gas to the outer zone; and the switching means may include a first open/close valve provided to the first raw material gas supply passage, a second open/close valve provided to the second raw material gas passage, a third open/close valve provided to the first oxidant gas supplying passage and a fourth open/close valve provided to the second oxidant gas supply passage.

Additionally, the raw material gas may be a mixture of a plurality of material gases, and the process gas supplying means may include: a plurality of material gas supplying passages; and an open/close valve provided to one of the material gas supplying passages so that the material gas supplied through the one of the material gas supplying passages is selectively added to the raw material gas.

The process chamber may include: a table on which the object is placed; and a vertical moving mechanism for moving the table in a vertical direction so that a distance between the table and the process gas introducing means is changeable. Accordingly, when the film deposition process is performed at a high vacuum so as to form crystalline nucleuses, the distance between the wafer and the shower head can be increased so that the raw material gas and the oxidant gas are uniformly mixed to each other by diffusion, which results in a uniform composition of the deposited film.

The film deposition apparatus according to the present invention may further comprise: pressure detecting means for detecting a pressure of each of the raw material gas and the oxidant gas in said process gas introducing means; dilution gas adding means for adding a dilution gas to one of the raw material gas and the oxidant gas; and dilution gas amount control means for controlling an amount of the dilution gas to be added based on the pressure detected by the pressure detecting means so that the pressures of the raw material gas and the oxidant gas in the process gas introducing means are substantially equal to each other. Accordingly, there is no pressure difference between the raw material gas and the oxidant gas in the process gas introducing means. Thus, there is

no leakage between the spaces provided with the raw material gas and the oxidant gas, and the raw material gas and the oxidant gas do not reversely flow into the process gas introducing means after exiting therefrom. Thus, the premature reaction of the raw material gas and the oxidant gas in the process gas introducing means can be prevented.

In one embodiment of the present invention, the process gas introducing means may comprise a showerhead having a plurality of raw material gas injection openings and a plurality of oxidant gas injection openings uniformly arranged on a bottom surface thereof, the bottom surface corresponding to the gas injection surface divided into the inner zone and the outer zone, the showerhead including: an inner raw material gas head space connected to the first raw material gas supply passage, a part of the injection openings located in the inner zone being connected to the inner raw material head space; an outer raw material gas head space connected to the second raw material gas supply passage, a part of the injection openings located in the outer zone being connected to the outer raw material head space; an inner oxidant gas head space connected to the first oxidant gas supply passage, a part of the injection openings located in the inner zone being connected to the inner oxidant gas head space; and an outer oxidant gas head space connected to the second oxidant gas supply passage, a part of the injection openings located in the outer zone being connected to the outer oxidant gas head space.

Additionally, there is provided according to another aspect of the present invention a film deposition method for forming a film on an object in a process chamber by introducing a raw material gas and an oxidant gas from a showerhead to the process chamber, the film

deposition method comprising: a first process of injecting a raw material gas to a first area directly above a center portion of the object and an oxidant gas to a second area directly above a peripheral portion of the object surrounding the center portion while maintaining the process chamber at a first predetermined vacuum; and a second process of injecting the raw material gas and the oxidant gas while maintaining the process chamber at a second predetermined vacuum lower than the first predetermined vacuum.

According to the above-mentioned invention, in the first process, crystalline nucleuses can be efficiently formed on the object to be processed such as a wafer by injecting the raw material gas to the center portion of wafer and the oxidant gas to the peripheral portion of the wafer surrounding the center portion while maintaining the process chamber at a high vacuum. After the crystalline nucleuses are formed on the wafer in the first process, the second process is performed. In the second process, the crystal of the film can be grown at a high rate by injecting the raw material gas and the oxidant gas uniformly to the entire surface of the wafer at a relatively low temperature while maintaining the process chamber at a relatively low vacuum.

Additionally, in the second process, the raw material gas and the oxidant gas may be uniformly injected to both the first area and the second area.

The film deposition method according to the present invention may further comprise vertically moving the object in the process chamber so that a distance between the showerhead and the object is changed between the first process and the second process. The distance in the first process may be set to be greater than the

distance in the second process. Accordingly, when the film deposition process is performed at a high vacuum in the first process so as to form crystalline nucleuses, the distance between the wafer and the shower head can be increased so that the raw material gas and the oxidant gas are uniformly mixed to each other by diffusion, which results in a uniform composition of the deposited film.

Additionally, the first and second processes may include detecting a pressure of each of the raw material gas and the oxidant gas, and adding a dilution gas to one of the raw material gas and the oxidant gas whichever has a higher pressure than the other so as to substantially equalize the pressures of the raw material gas and the oxidant gas. Accordingly, there is no pressure difference between the raw material gas and the oxidant gas in the showerhead. Thus, there is no leakage between the spaces provided with the raw material gas and the oxidant gas in the shower head, and the raw material gas and the oxidant gas do not reversely flow into the showerhead after exiting therefrom. Thus, the premature reaction of the raw material gas and the oxidant gas in the showerhead can be prevented.

In one embodiment of the present invention to deposit a PZT film, the raw material gas supplied in the second process may be an organometallic mixture gas containing $\text{Pb}(\text{DPM})_2$, at least one of $\text{Zr}(\text{t-OC}_4\text{H}_9)_4$, $\text{Zr}(\text{DPM})_4$, $\text{Zr}(\text{i-OC}_3\text{H}_7)_4$, $\text{Zr}(\text{C}_5\text{H}_7\text{O}_2)_4$ and $\text{Zr}(\text{C}_5\text{HF}_6\text{O}_2)_4$ and at least one of $\text{Ti}(\text{i-OC}_3\text{H}_7)_4$ and $\text{Ti}(\text{i-OC}_3\text{H}_7)_2(\text{DPM})_2$; the raw material gas in the first process may be the organometallic mixture gas lacking the Zr material gas; and the oxidant gas supplied in the first and second processes may be at least one selected from a group consisting of NO_2 , O_2 , O_3 and N_2O .

Additionally, the first predetermined vacuum may

be equal to or lower than 100 mTorr, and the second predetermined vacuum may be higher than 100 mTorr.

Other objects, features and advantages of the present invention will become more apparent from the following detailed description when read in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF DRAWINGS

FIG. 1 is a structural diagram of a film deposition apparatus according to a first embodiment of the present invention;

FIG. 2 is a plan view of a showerhead provided in the film deposition apparatus shown in FIG. 1;

FIG. 3 is a cross-sectional view of the showerhead shown in FIG. 1;

FIG. 4A is an illustration for explaining gas flow in a first process; FIG. 4B is an illustration for explaining gas flow in a second process;

FIG. 5 is an illustration of a crystal nucleus and a PZT film formed on the crystal nucleus;

FIG. 6 is an illustration for explaining a small gap formed between adjacent head spaces in a showerhead body;

FIG. 7 is a cross-sectional view of a process gas introducing part provided in a film deposition apparatus according to a second embodiment of the present invention;

FIG. 8 is a plan view of a top plate of the process gas introducing part shown in FIG. 7;

FIG. 9 is a cross-sectional view of a process gas introducing part provided in a film deposition apparatus according to a third embodiment of the present invention;

FIG. 10 is a cross-sectional view taken along a line X-X of FIG. 9;

FIG. 11 is a cross-sectional view of a process gas introducing part provided in a film deposition apparatus according to a fourth embodiment of the present invention;

FIG. 12 is a cross-sectional view of a process gas introducing part provided in a film deposition apparatus according to a fifth embodiment of the present invention; and

FIG. 13 is a plan view of a gas-introducing pipe shown in FIG. 12.

BEST MODE FOR CARRYING OUT THE INVENTION

The inventors made the present invention based on the discovery that a good quality PZT film can be formed at a high deposition rate at a low temperature by initially supplying a raw material gas from the center of a showerhead and supplying an oxidant gas around the raw material gas so as to form crystalline nucleuses under a high vacuum environment, and thereafter growing the crystal of the PZT film in a state in which the raw material gas and the oxidant gas are uniformly supplied from the entire surface of the showerhead.

A description will now be given, with reference to FIGS. 1 to 6, of a first embodiment of the present invention. FIG. 1 is a structural diagram of a film deposition apparatus according to the first embodiment of the present invention. FIG. 2 is a plan view of a showerhead provided in the film deposition apparatus shown in FIG. 1, viewed from the bottom side. FIG. 3 is a cross-sectional view of the showerhead shown in FIG. 1.

In the present embodiment, $\text{Pb}(\text{DPM})_2$, $\text{Zr}(\text{t-OC}_4\text{H}_9)_4$

and $\text{Ti}(\text{I-OC}_3\text{H}_7)_4$ are used as material gases, which are mixed with each other so as to prepare the raw material gas, and NO_2 gas is used as an oxidant gas so as to deposit a PZT film.

5 The film deposition apparatus 2 shown in FIG. 1 comprises a cylindrical process chamber 4 made of aluminum. In the center of a bottom 6 of the process chamber 4, an opening 8 is formed so as to provide a power supply line. A plurality of exhaust openings 16 are formed in the
10 periphery of the bottom 6. The exhaust openings 16 are connected to a vacuum line 14 including a turbomolecular pump 10 and a dry pump 12 so as to evacuate gases in the process chamber 4. The exhaust openings 16 are arranged along a circumference of the bottom 6 at equal intervals.

15 A disc-like table 18 made of a non-conductive material such as alumina is provided in the process chamber 4. The table 18 includes a leg portion 20 having a hollow cylindrical shape. The leg portion 20 extends downward from the center of the bottom of the table 18.
20 The bottom end of the leg portion 20 is connected to the bottom 6 of the process chamber 4 via a bellows 160 and a seal member such as an O-ring (not shown in the figure). The bellows 160 and the O-ring are provided to allow the vertical movement of the table 18 while the interior of
25 the leg portion 20 is hermetically separated from the space inside the process chamber 4.

 The table 18 is mounted to an end of a shaft 162 which is movable up and down by a vertical moving mechanism (not shown in the figure). A distance between
30 the table 18 and a showerhead 50 provided above the table 18 can be varied by the vertical movement of the table 18. It should be noted that the showerhead 50 may be vertically moved instead of the table 18.

The table 18 has a heating means. Specifically, a resistance heater 22 made of carbon coated with SiC is incorporated in the table 18. The heater 22 can heat a semiconductor wafer W placed on the table 18 to a desired temperature.

An insulated power supply lead wire 28 is connected to the heater. The lead wire 28 passes through inside the leg portion 20 and the opening 8 so as to extend to outside the process chamber 4. The lead wire 28 is connected to a power source 32 via a switch 30. It should be noted that a heating lamp such as a halogen lamp may be used instead of the resistance heater 22 so as to heat the wafer W on the table 18.

A plurality of lifter openings 40 are provided in the periphery of the table 18, each of which extends in the vertical direction. A wafer lifter pin 48 is accommodated in each of the lifter openings 40 so as to support and lift the wafer W when the wafer W is loaded to or unloaded from the process chamber 4 by being vertically moved by a lifter pin moving mechanism (not shown in the figure). Normally, the wafer W is supported by three lifter pins 40.

A top plate 51 is mounted to the top of the process chamber 4 via an O-ring 53 so as to hermetically seal the process chamber 4. The showerhead 50 is mounted on the top plate 51 so that the showerhead 50 serves as a process gas introducing means. The showerhead 50 is located opposite to the table 18 so as to cover the entire top surface of table 18. A process space S is formed between the showerhead 50 and the table 18.

The showerhead 50 is provided to introduce the raw material gas and the oxidant gas into the process chamber 4. A plurality of raw material gas injection

openings 52 and a plurality of oxidant gas injection openings 54 are formed in a gas injection surface 57 provided on the bottom of a showerhead body 55 of the showerhead 50.

5 As shown in FIG. 2, the injection openings 52 and 54 are uniformly distributed on the entire gas injection surface 57. In FIG. 2, the diameter of each of the injection openings 52 is larger than the diameter of each of the injection openings 54 for the sake of easy
10 recognition of each of the injection openings 52 and 54. However, the diameter of each of the injection openings 52 and 54 may be equal to each other, or the diameter of each of the injection openings 54 may be larger than the diameter of each of the injection openings 52.

15 The interior of the showerhead body 55 is separated into a raw material gas head space 56 and an oxidant gas head space 58.

 The raw material gas head space 56 includes inner raw material gas head spaces 56A and outer raw
20 material gas head spaces 56B. The inner raw material gas head spaces 56A are formed as concentric annular spaces, and the outer raw material gas head spaces 56B are also formed as concentric annular spaces surrounding the inner raw material gas head spaces 56A. The inner raw material
25 gas head spaces 56A communicate with each other by passages (not shown in the figure), and the outer raw material gas head spaces 56b communicate with each other by passages (not shown in the figure)

 Similarly, the oxidant gas head space 58
30 includes inner oxidant gas head space 58A and outer oxidant gas head space 58B. The inner oxidant gas head space 58A is formed in the center of the showerhead body 55, and the outer oxidant gas head space 58B is formed as

an annular space surrounding the inner oxidant gas head space 58A.

Accordingly, the interior of the showerhead body 55 is divided into four spaces 56A, 56B, 58A and 58B. It should be noted that the configuration and arrangement of the four spaces is not limited to that shown in FIG. 3, and other configuration and arrangement may be used.

The inner raw material gas head spaces 56A are connected to a first raw material gas supply passage 62 via a gas introduction port 60. The outer raw material gas head spaces 56B are connected to a second raw material gas supply passage 66 via a gas introduction port 64. A first open/close valve 67A is provided in the middle of the passage 62, and a second open/close valve 67B is provided in the middle of the passage 66.

The first and second raw material gas supply passages 62 and 66 are merged, and, then, branched into three branch passages 68A, 68B and 68C. The branch passages 68A, 68B and 68C are connected to flow controllers such as mass-flow controllers 70A, 70B and 70C, respectively, so that the material gases $\text{Pb}(\text{DPM})_2$, $\text{Zr}(\text{t-OC}_4\text{H}_9)_4$ and $\text{Ti}(\text{I-OC}_3\text{H}_7)_4$ are supplied at predetermined flow rates, respectively.

Accordingly, the three kinds of gases are mixed to each other to produce the raw material gas in the middle of the passage, and the raw material gas is selectively supplied to the inner raw material gas head spaces 56A and the outer raw material gas head spaces 56B as described later. It should be noted that a tape heater (not shown in the figure) is wound on each of the first and second raw material gas supply passages 62 and 66 and the branch passages 68A, 68B and 68C so as to prevent the gases from being liquidized. Additionally, the branch

passage 68 is provided with a fifth open/close valve 67E so as to control the supply of the Zr material gas.

Additionally, the inner oxidation gas head space 58A is connected to a first oxidation gas supply passage 74 via a gas introduction port 72, and the outer oxidation gas head space 58B is connected to a second oxidation gas supply passage 74 via a gas introduction port 72. A third and fourth open/close valves 67C and 67D are provided in the middle of the first and second oxidant gas supply passages 74 and 78, respectively.

The first and second oxidant gas supply passages 74 and 78 are merged to a passage 80. A flow controller such as a mass-flow controller 82 is provided to the passage 80 so as to selectively supply the NO₂ gas to the inner and outer oxidant gas head spaces 58A and 58B at a predetermined flow rate as described later.

Each of the injection openings 52 for injecting the raw material gas communicates with either the inner raw material gas head spaces 56A or the outer raw material gas head spaces 56B. Each of the injection openings for injecting the oxidant gas communicates with either the inner oxidant gas head space 58A or the outer oxidant gas head space 58B. Specifically, as shown in FIG. 2, the gas injection surface 57 is divided into two zones, one is an inner zone 84 and the other is an outer zone 86. the inner zone 84 is located in the center of the gas injection surface 57. The outer zone 86 has an annular shape so as to surrounds the inner zone 84. In FIG. 2, the boundary between the inner zone 84 and the outer zone is indicated by a single dashed chain line 88.

The gas injection openings 52A arranged within the inner zone 84 are connected to the inner raw material gas head spaces 56A, and the gas injection openings 52B

arranged within the outer zone 86 are connected to the outer raw material gas head spaces 56B. The gas injection openings 54A arranged within the inner zone 84 are connected to the inner oxidant gas head space 58A, and the gas injection openings 54B arranged within the outer zone 86 are connected to the outer oxidant gas head space 58B.

According to the above-mentioned structure, at the initial stage of the film deposition process in which the process chamber is maintained at a high vacuum to form a crystalline nucleus, the raw material gas lacking Zr material is introduced into the process chamber 4 from the gas injection openings 52A located in the inner zone 84, and the oxidant gas is introduced into the process chamber 4 from the gas injection openings 52B located in the outer zone 86. On the other hand, after the pressure of the process chamber 4 is changed to a low vacuum, the raw material gas and the oxidant gas are introduced from the entire gas injection surface 57 of the showerhead 50. In order to achieve such a gas introduction process during the film deposition process, a valve open/close control means 90 is provided to control the operation of each of the first to fifth open/close valves 67A, 67B, 67C, 67D and 67E.

The inner raw material gas head spaces 56A and the outer raw material gas head spaces 56B are provided with capacitor manometers 92A and 92B as a pressure detecting means, respectively, so as to detect a pressure inside the respective spaces. Similarly, the inner oxidant gas head space 58A and the outer oxidant gas head space 58B are provided with capacitor manometers 92C and 92D as a pressure detecting means, respectively, so as to detect a pressure inside the respective spaces. The output of each of the manometers 92A to 92D is supplied to

a dilution gas introducing amount control means 94, which is achieved by a microcomputer.

The first and second raw material gas supply passages 62 and 66 are connected to an inner gas passage 96, and the first and second oxidant gas supply passages 74 and 78 are connected to an inert gas passage 98. Each of the inert gas passages serves as a dilution gas introducing means to supply N_2 gas which is an inert gas as a dilution gas. The inert gas passages 96 and 98 are provided with flow controller 100 and 102 such as mass-flow controllers, respectively, so as to control the flow rate of the inert gas to an appropriate value in accordance with the control of the dilution gas introduction control means 94.

A description will now be given of the film deposition process performed by the film deposition apparatus 2 having the above-mentioned structure.

The semiconductor wafer W to be processed is conveyed to the process chamber 4 that is maintained at a vacuum, and the wafer W is placed on the table 18. Then, the wafer W is heated by the resistance heater 22 to be a predetermined process temperature. Thereafter, the film deposition process is started by introducing the raw material gas and the oxidant gas into the process chamber 4 from the showerhead 50 while maintaining the process chamber 4 at a predetermined process pressure.

The raw material gas is a mixture gas prepared by mixing gases, which are prepared by evaporating liquidized $Pb(DPM)_2$, $Zr(t-OC_4H_9)_4$ and $Ti(I-OC_3H_7)_4$, by flowing at predetermined flow rates, respectively. In the first process which is performed under a first vacuum environment to form the crystalline nucleus, the flow rates of the Pb, Zr and Ti material gases are controlled

to be within the ranges of 0.1 to 10 sccm, 0 sccm (no gas flow) and 0.1 to 10 sccm, respectively. In the second process which is performed under a second vacuum environment to grow the crystal, the flow rates of the Pb, Zr and Ti material gases are controlled to be within the ranges of 0.1 to 10 sccm, 0.1 to 10 sccm and 0.1 to 10 sccm, respectively.

The raw material gas (mixture gas) supplied to the showerhead 50 via the first and second raw material gas supply passages 62 and 66 flows into the respective inner and outer raw material gas head spaces 56A and 56B. Thereafter, the raw material gas is introduced into the process chamber 4 via the gas injection openings 52 (52A and 52B) provided on the gas injection surface 57.

On the other hand, the NO₂ gas supplied to the showerhead 50 via the first and second oxidant gas passages 74 and 78 flows into the inner and outer oxidant gas head spaces 58A and 58B, respectively. Thereafter, the oxidant gas is introduced into the process chamber 4 via the gas injection openings 54 (54A and 54B) provided on the gas injection surface 57.

The raw material gas and the NO₂ gas introduced into the process space S in the process chamber 4 are mixed in the process space S and react with each other, which deposit the crystalline nucleus of the PTO film or the PZT film on the wafer W by the CVD action.

In the present embodiment, the film deposition process includes the first process for forming the crystalline nucleus of the PTO film under a high vacuum, and the second process for depositing the PZT film on the crystalline nucleus at a high deposition rate under a relatively low vacuum. Specifically, in the first process, only the raw material gas (lacking Zr material gas) is

injected into the process chamber 4 from the inner zone 84 as indicated by thick arrows in FIG. 4A, and only the oxidant gas is introduced into the process chamber 4 from the outer zone 86 as indicated by thin arrows in FIG. 4A.

5 On the other hand, in the second process, the raw material gas (containing the Zr material gas) and the oxidant gas are uniformly injected into the process chamber 4 from the entire gas injection surface 57 (both the inner zone 84 and the outer zone 86) as indicated by thick and thin
10 arrows in FIG. 4B.

More specifically, referring to FIG. 3, when the first process is performed, the second, third and fifth open/close valves 67B, 67C and 67E are closed and the first and fourth open/close valves 67A and 67D are open by
15 the control of the valve control means 90 so as to supply ~~the raw material gas~~ (lacking Zr material gas) to the inner raw material gas head spaces 56A and supply the oxidant gas to the outer oxidant gas head space 58B. Thereby, the raw material gas (lacking Zr material gas) is
20 introduced into the process space S from the injection openings 52A in the inner zone 84, and the oxidant gas is introduced into the process space S from the injection openings 54B in the outer zone 86.

In the first process, the process temperature is
25 in the range from 400°C to 450°C, and the process pressure is a high vacuum such as less than 100 mTorr, preferably 10 mTorr. As mentioned above, by supplying only the raw material gas (lacking Zr material gas) from the center portion of the showerhead body 55 and supplying the
30 oxidant gas so as to surrounds the raw material gas, the crystalline nucleus of the PTO film can be formed on the wafer W under a high vacuum.

Additionally, in the first process performed

under the high vacuum, a distance between the wafer W and the showerhead 50 is increased by operating the drive shaft 162 (drive mechanism) so as to vertically move the table 18. The distance between the wafer W and the showerhead 50 is in the range from 20 mm to 150 mm. In the high vacuum environment, the raw material gas and the oxidant gas reach the wafer W according to diffusion (molecular flow). Accordingly, the raw material gas and the oxidant gas diffuses more sufficiently as the distance between the showerhead 50 and wafer W increases, which improves uniformity of the deposited film. Additionally, since the pressure distribution under the high vacuum environment is relatively uniform, the efficiency of material usage can be maintained unchanged even if the distance between the showerhead 50 and the wafer W is varied.

After the crystalline nucleus of the PTO film is formed in the first process, the operation proceeds to the second process, which is performed under the second vacuum environment.

When the second process is performed, all the first to fifth open/close valves 67A to 67E are open so as to introduce the raw material gas (containing Zr material gas into the inner and outer raw material gas head spaces 56A and 56B and the oxidant gas into the inner and outer oxidant gas head spaces 58A and 58B. Thereby, the raw material gas is injected from all of the injection openings 52A and 52B, and the oxidant gas is injected from all of the injection openings 54A and 54B. Accordingly, both the raw material gas and the oxidant gas are uniformly injected from the entire injection surface 57 of the showerhead 50.

In the second process, the process temperature

is in the range from 400°C to 450°C, and the process pressure is a relatively low vacuum such as greater than 100 mTorr, preferably in the range from 100 mTorr to 1000 mTorr.

5 Additionally, in the second process performed under the relatively low vacuum, a distance between the wafer W and the showerhead 50 must be smaller than that in the first process performed under the high vacuum environment. Specifically, the distance between the wafer
10 W and the showerhead 50 is in the range from 5 mm to 30 mm. In the low vacuum environment, the raw material gas and the oxidant gas reach the wafer W according to viscous flow. Accordingly, the efficiency of usage of the raw material gas and the oxidant gas decreases as the distance
15 between the showerhead 50 and wafer W increases. This means that the efficiency of usage of the raw material gas and the oxidant gas increases as the distance between the showerhead 50 and wafer W decreases, which increases a film deposition rate

20 Additionally, according to the showerhead 50 having the above-mentioned design structure, the gases injected from the showerhead 50 form a stratified flow in the low vacuum environment. Accordingly, the uniformity in the deposited film rarely deteriorates when the
25 distance between the showerhead 50 and the wafer W is small. Additionally, in the low vacuum environment, a gas layer having a thickness of less than several millimeters, which is referred to as a boundary layer, is formed above the wafer surface. The intensity of gases in the boundary
30 layer increases as the distance between the showerhead 50 and the wafer W decreases. Accordingly, the film deposition rate increases as the distance between the showerhead 50 and the wafer W decreases.

The crystal of the PZT film normally grows at a temperature of about 600°C. However, as mentioned above, the formation of the crystal nucleus comprising the oxide of Pb and Ti on the wafer W allows deposition of the PZT film at a high deposition rate at a relatively low temperature ranging from 400°C to 450°C due to the influence by the PTO crystalline nucleus.

Thereby, the PZT film can be deposited at a high deposition rate on the crystal nucleus formed in the first process. Additionally, the uniformity of each element in the deposited PZT film can be very high. The thus-formed PZT film has a perovskite structure of $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$. FIG. 5 is an illustration of the crystal nucleus and the PZT film formed on the crystal nucleus. As shown in FIG. 5, a plurality of PTO crystal nuclei 112 are formed on the wafer W in the first process, and, then, the PZT film 114 grows on the PTO crystal nuclei 112 in the second process.

Additionally, in the present embodiment, a pressure in each of the head spaces 56A, 56B, 58A and 58B is maintained unchanged so that the raw material gas and the oxidant gas do not leak within the showerhead body 55 or the raw material gas and the oxidant gas do not reverse flow into the showerhead body 55. The showerhead body 55 is fabricated by joining aluminum blocks each of which has cavities corresponding to the head spaces and the gas passages. It is inevitable to completely eliminate a small gap between the joined portions of the aluminum blocks even if the aluminum blocks are machined with very high accuracy.

Accordingly, if, for example, a large pressure difference is generated between the raw material gas head space 56 and the oxidant gas head space 58, one of the raw

material gas and the oxidant gas leaks through the small gap, which results in mixture of the raw material gas and the oxidant gas within the showerhead body 55. In such a case, particles may be formed by the reaction of the raw material gas with the oxidant gas. Such a phenomenon may also occur if one of the raw material gases reversely flows into the injecting openings corresponding to the other gas.

In order to eliminate such a problem, in the present embodiment, the pressure in each of the head spaces 56A, 56B, 58A and 58B is detected by the respective one of the capacitor manometers 92A to 92D so as to control the pressures in the head spaces 56A, 56B, 58A and 58B are substantially equal to each other by adding the dilution gas (N_2 gas). In this case, the pressure difference between the head spaces is not required to be accurately controlled to zero, and there is no problem if the pressure difference is maintained to be less than 10%. As mentioned above, by appropriately supplying N_2 dilution gas to the space of which pressure is lower than the pressure in the adjacent space, the pressure difference between the spaces can be substantially eliminated. Thus, the gas leakage within the showerhead body 55 can be prevented, and the reverse flow of the injected gas to the showerhead body 55 can also be prevented.

FIG. 6 is an illustration for explaining the small gap formed between adjacent head spaces in the showerhead body 55. In a case in which the showerhead body 55 is formed by joining an upper block and a lower block each of which has a cavity to define the raw material gas head space 56 and the oxidant gas head space 58, a small gap 116 is formed between the blocks A and B. If there is a difference between the pressure P_1 in the

head space 56 and the pressure P2, the gas in one of the head spaces 56 and 59 leaks to the other. In the present embodiment, the pressure difference can be substantially eliminated by supplying the N₂ dilution gas to one of the head spaces 56 and 58 so as to maintain the pressure P1 and pressure P2 to be substantially equal to each other. Accordingly, the gas leakage between the head spaces 56 and 58 can be prevented. It should be noted that the dilution gas is not limited to the N₂ gas, and other gases such as He gas or Ar gas may be used.

A shown in FIG. 2, the size (diameter) of the gas injection surface 57 is set to be within plus or minus 10% with respect to the wafer W. In this case, the diameter of the inner zone 84 is preferably in a range from 10% to 70% of the effective diameter of the gas injection surface 57.

A description will now be given, with reference to FIGS. 7 and 8, of a second embodiment of the present invention. FIG. 7 is a cross-sectional view of a process gas introducing part provided in the film deposition apparatus according to the second embodiment of the present invention. FIG. 8 is a plan view of a top plate of the process gas introducing part shown in FIG. 7.

The structure of the film deposition apparatus according to the second embodiment of the present invention is the same as the film deposition apparatus 2 shown in FIG. 1 except for the process gas introducing part shown in FIG. 7, and descriptions thereof will be omitted.

In the present embodiment, a showerhead 120 as a first process gas introducing means is attached to a top plate 51 of the process chamber 4. The showerhead 120 has a mounting portion 120A protrudingly formed in the center

thereof. The mounting portion 120A is mounted to the top plate 51 of the process chamber 4, and a plurality of process gas supply passages 122 as a process gas introducing means are provided around the mounting portion 120A. The showerhead 120 and the process gas supply passages 122 together constitute a process gas introducing means 124. The showerhead 120 has a bell-jar shape having a single interior space. A plurality of injection openings 128 are formed in a gas injection surface 126.

One of the raw material gas or the oxidant gas is supplied to the showerhead 120. In FIG. 7, the raw material gas is supplied to the showerhead 120.

The gas introducing means 122 includes a plurality of gas openings 130 arranged around the mounting portion 120A at substantially equal intervals so that the NO_2 gas as the oxidant gas is injected toward the process space S. In this case, the diameter L1 of a circle along which the gas openings are arranged is smaller than the diameter of the showerhead 120 so that a top plate of the showerhead 120 serves as a baffle plate, when the oxidant gas is injected, so as to promote the diffusion of the oxidant gas.

In the present embodiment, the PZT raw material gas is injected from the showerhead 120 to the process space S, and the oxidant gas is injected from the gas openings 130 of the gas introducing means 122 provided around the showerhead 120. Thereby, a PZT film having high uniformity of compositions can be deposited on the wafer W. Additionally, the structure of the process gas introducing means 124 can be simplified, and there is no leak within the showerhead 120. Further, since the structure of the process gas introducing means is simple, other mechanism such as a cooling mechanism, a heating

mechanism or a high-frequency mechanism can be easily incorporated into the process chamber 4.

A description will now be given, with reference to FIGS. 9 and 10, of a third embodiment of the present invention. FIG. 9 is a cross-sectional view of a process gas introducing part provided in a film deposition apparatus according to the third embodiment of the present invention. FIG. 10 is a cross-sectional view taken along a line X-X of FIG. 9.

The structure of the film deposition apparatus according to the third embodiment of the present invention is the same as the film deposition apparatus 2 shown in FIG. 1 except for the process gas introducing part 132 shown in FIG. 9, and descriptions thereof will be omitted. It should be noted that the process gas introducing part 132 has the showerhead 120 of the above-mentioned second embodiment.

In the present embodiment, the mounting portion 120A of the showerhead 120 has an elongated shape. Additionally, a second gas introducing means 134 includes an outer cylinder 136 that surrounds the mounting portion 120A so as to form a double tube structure. The mounting portion 120A is mounted to a top plate of the outer cylinder 136. The diameter of the bottom opening of the outer cylinder 136 is smaller than the diameter of the showerhead 120 so that the top plate of the showerhead 120 serves as a baffle plate.

According to the present embodiment, a PZT film having high uniformity of compositions can be deposited on the wafer W. Additionally, the structure of the process gas introducing means 132 is simple, and there is no leak within the showerhead 120.

A description will now be given, with reference

to FIG. 11, of a fourth embodiment of the present invention. FIG. 11 is a cross-sectional view of a process gas introducing part provided in a film deposition apparatus according to the fourth embodiment of the present invention.

The structure of the film deposition apparatus according to the fourth embodiment of the present invention is the same as the film deposition apparatus 2 shown in FIG. 1 except for the process gas introducing part 140 shown in FIG. 11, and descriptions thereof will be omitted. It should be noted that the process gas introducing part 140 has the showerhead 120 of the above-mentioned second embodiment.

In the present embodiment, the process gas introducing part 140 comprises the bell-jar type showerhead 120 as a first gas introducing means and a second gas introducing means 142 provided around the showerhead 120. The gas introducing means 142 includes an annular separation plate that connect the side wall of the showerhead 120 and the side wall of the process chamber 4 so as to form a separate showerhead defined by the annular plate 144 and the side wall and the top plate of the process chamber 4. A plurality of gas openings 146 are provided in the annular plate 144 so that the NO₂ gas is injected from the gas openings 146 toward the process space S.

According to the present embodiment, a PZT film having high uniformity of compositions can be deposited on the wafer W. Additionally, the structure of the process gas introducing part 140 is simple, and there is no leak within the showerhead 120.

A description will now be given, with reference to FIGS. 12 and 13, of a fifth embodiment of the present

invention. FIG. 12 is a cross-sectional view of a process gas introducing part provided in a film deposition apparatus according to the fifth embodiment of the present invention. FIG. 13 is a plan view of a gas introducing pipe shown in FIG. 12.

The structure of the film deposition apparatus according to the fifth embodiment of the present invention is the same as the film deposition apparatus 2 shown in FIG. 1 except for the process gas introducing part 150 shown in FIG. 12, and descriptions thereof will be omitted. It should be noted that the process gas introducing part 150 has the showerhead 120 of the above-mentioned second embodiment.

In the present embodiment, the process gas introducing part 150 comprises the bell-jar type showerhead 120 and a gas introducing means 152 provided around the showerhead 120. The gas introducing means 152 includes a ring-like gas introducing pipe 154 mounted on the top plate 51 of the process chamber 4. A plurality of gas openings 156 are provided along the gas introducing pipe 154 at substantially equal intervals so that the NO_2 gas is injected from the gas openings 156 toward the process space S.

According to the present embodiment, a PZT film having high uniformity of compositions can be deposited on the wafer W. Additionally, the structure of the process gas introducing part 150 is simple, and there is no leak within the showerhead 120.

In the above-mentioned embodiments, a 6-inch wafer is used. However, the size of the wafer W is not limited to 6 inches, and other size wafers such as 8-inch wafer or 12-inch wafer may be used. In such a case, the diameter of the inner zone 84 may be increased in response

to the increase in the wafer diameter.

Additionally, although $\text{Zr}(\text{t-OC}_4\text{H}_9)_4$ is used as the Zr material to form the PZT film in the above-mentioned embodiments, other Zr materials such as $\text{Zr}(\text{DPM})_4$,
5 $\text{Zr}(\text{i-OC}_3\text{H}_7)_4$, $\text{Zr}(\text{C}_5\text{H}_7\text{O}_2)_4$ or $\text{Zr}(\text{C}_5\text{HF}_6\text{O}_2)_4$ and a combination of two or more of the aforementioned may be used. Further, although $\text{Ti}(\text{i-OC}_3\text{H}_7)_4$ is used as the Ti material in the above-mentioned embodiments, other Ti materials such as $\text{Ti}(\text{i-OC}_3\text{H}_7)_2(\text{DPM})_2$ may be used.

10 Additionally, although the PZT film as a dielectric film is deposited by the film deposition apparatus according to the above-mentioned embodiments, the present invention is not limited to the deposition of the PZT film, and other films such as a $\text{BaSr}_{1-x}\text{Ti}_x\text{O}_3$ film
15 may be deposited by using other organometallic materials.

Further, the oxidant gas is not limited to NO_2 gas, and other gases such as O_2 , O_3 or N_2O and a combination of two or more of the aforementioned may be used. Additionally, the object to be processed is not
20 limited to the semiconductor wafer, and other object such as an LCD substrate or a glass substrate may be used.

The present invention is not limited to the specifically disclosed embodiments, and variations and modifications may be made without departing from the scope
25 of the present invention.

The present application is based on Japanese priority patent application No. 11-245836 filed on August 31, 1999, the entire contents of which are hereby incorporated by reference.

30

CLAIMS

1. A film deposition apparatus (2) for depositing a film on an object (W) to be processed, the
5 film deposition apparatus (2) comprising:
a process chamber (4) accommodating the object (W) therein;
process gas supplying means (74, 78, 80, 68A-68C, 82, 70A-70C) for supplying process gases including a raw
10 material gas and an oxidant gas;
evacuating means (10-14) for evacuating the process gases from said process chamber (4) so as to maintain said process chamber (4) to be at a predetermined vacuum; and
15 process gas introducing means (50) for introducing the process gases supplied from said process gas supplying means into said process chamber (4),
wherein said process gas introducing means (50) is configured and arranged to inject the process gases
20 toward an entire surface of the object (W), a gas injecting surface from which the process gases are injected being divided into an inner zone (84) covering a center portion of the object (W) and an outer zone (86) surrounding the inner zone (84); and
25 said process gas supplying means (74, 78, 80, 68A-68C, 82, 70A-70C) selectively supplies the process gases to said process gas introducing means (50) so that the raw material gas is separately injected from said inner zone (84) and said outer zone (86) and the oxidant
30 gas is separately injected from said inner zone (84) and said outer zone (86).

2. The film deposition apparatus as claimed in

claim 1, wherein said process gas supplying means includes switching means (67A-67D, 90) for switching the supply of the raw material gas to said process gas introducing means (50) so that the raw material gas is selectively injected from either said inner zone (84) alone or both said inner zone (84) and said outer zone (86), and the oxidant gas is selectively injected from either said outer zone (86) alone or both said inner zone (84) and said outer zone (86).

10

3. The film deposition apparatus as claimed in claim 2, wherein said process gas supplying means includes a first raw material gas supply passage (62) supplying the raw material gas to said inner zone (84), a second raw material gas supply passage (66) supplying the raw material gas to said outer zone (84), a first oxidant gas supply passage (74) supplying the oxidant gas to said inner zone (84) and a second oxidant gas supply passage (78) supplying the oxidant gas to said outer zone (86);

20 and

said switching means includes a first open/close valve (67A) provided to said first raw material gas supply passage (62), a second open/close valve (67B) provided to said second raw material gas passage (66), a third open/close valve (67C) provided to said first oxidant gas supplying passage (74) and a fourth open/close valve provided to said second oxidant gas supply passage (78).

4. The film deposition apparatus as claimed in claim 1, wherein the raw material gas is a mixture of a plurality of material gases, and said process gas supplying means includes:

a plurality of material gas supplying passages

(68A-68C); and

an open/close valve (67E) provided to one of
said material gas supplying passages (68A-68C) so that the
material gas supplied through said one of said material
5 gas supplying passages (68A-68C) is selectively added to
the raw material gas.

5. The film deposition apparatus as claimed in
claim 1, wherein said process chamber (4) includes:

10 a table (18) on which the object (W) is placed;
and

a vertical moving mechanism (162) for moving
said table (18) in a vertical direction so that a distance
between said table and said process gas introducing means
15 (50) is changeable.

6. The film deposition apparatus as claimed in
claim 1, further comprising:

pressure detecting means (92A-92D) for detecting
20 a pressure of each of the raw material gas and the oxidant
gas in said process gas introducing means;

dilution gas adding means (96, 98, 100, 102) for
adding a dilution gas to one of the raw material gas and
the oxidant gas; and

25 dilution gas amount control means (94) for
controlling an amount of the dilution gas to be added
based on the pressure detected by said pressure detecting
means (92A-92D) so that the pressures of the raw material
gas and the oxidant gas in said process gas introducing
30 means are substantially equal to each other.

7. The film deposition apparatus as claimed in
claim 3, wherein said process gas introducing means

comprises a showerhead (50) having a plurality of raw material gas injection openings (52) and a plurality of oxidant gas injection openings (54) uniformly arranged on a bottom surface thereof, said bottom surface

5 corresponding to said gas injection surface divided into said inner zone (84) and said outer zone (86), said showerhead (50) includes:

an inner raw material gas head space (56A) connected to said first raw material gas supply passage (62), a part of said injection openings (52A) located in said inner zone (84) being connected to said inner raw material head space (56A);

an outer raw material gas head space (56B) connected to said second raw material gas supply passage (66), a part of said injection openings (52B) located in said outer zone (86) being connected to said outer raw material head space (56B);

an inner oxidant gas head space (58A) connected to said first oxidant gas supply passage (74), a part of said injection openings (54A) located in said inner zone (84) being connected to said inner oxidant gas head space (58A); and

an outer oxidant gas head space (58B) connected to said second oxidant gas supply passage (78), a part of said injection openings (54B) located in said outer zone (86) being connected to said outer oxidant gas head space (58B).

8. A film deposition method for forming a film on an object (W) in a process chamber (4) by introducing a raw material gas and an oxidant gas from a showerhead to said process chamber 4, the film deposition method comprising:

a first process of injecting a raw material gas to a first area directly above a center portion of the object (W) and an oxidant gas to a second area directly above a peripheral portion of the object (W) surrounding
5 said center portion while maintaining the process chamber (4) at a first predetermined vacuum; and

a second process of injecting the raw material gas and the oxidant gas while maintaining the process chamber (4) at a second predetermined vacuum lower than
10 the first predetermined vacuum.

9. The film deposition method as claimed in claim 8, wherein, in the second process, the raw material gas and the oxidant gas are uniformly injected to both
15 said first area and said second area.

10. The film deposition method as claimed in claim 8, further comprising vertically moving the object (W) in said process chamber (4) so that a distance between
20 said showerhead and the object (W) is changed between the first process and the second process.

11. The film deposition method as claimed in claim 10, wherein said distance in the first process is
25 set to be greater than said distance in the second process.

12. The film deposition method as claimed in claim 8, wherein the first and second processes includes detecting a pressure of each of the raw material gas and
30 the oxidant gas, and adding a dilution gas to one of the raw material gas and the oxidant gas whichever has a higher pressure than the other so as to substantially equalize the pressures of the raw material gas and the

oxidant gas.

13. The film deposition method as claimed in claim 9, wherein the raw material gas supplied in the second process is an organometallic mixture gas containing $\text{Pb}(\text{DPM})_2$, at least one of $\text{Zr}(\text{t-OC}_4\text{H}_9)_4$, $\text{Zr}(\text{DPM})_4$, $\text{Zr}(\text{i-OC}_3\text{H}_7)_4$, $\text{Zr}(\text{C}_5\text{H}_7\text{O}_2)_4$ and $\text{Zr}(\text{C}_5\text{HF}_6\text{O}_2)_4$ and at least one of $\text{Ti}(\text{i-OC}_3\text{H}_7)_4$ and $\text{Ti}(\text{i-OC}_3\text{H}_7)_2(\text{DPM})_2$; the raw material gas in the first process is the organometallic mixture gas lacking the Zr material gas; and the oxidant gas supplied in the first and second processes is at least one selected from a group consisting of NO_2 , O_2 , O_3 and N_2O .

14. The film deposition method as claimed in claim 13, wherein the first predetermined vacuum is equal to or lower than 100 mTorr, and the second predetermined vacuum is higher than 100 mTorr.

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FIG. 1

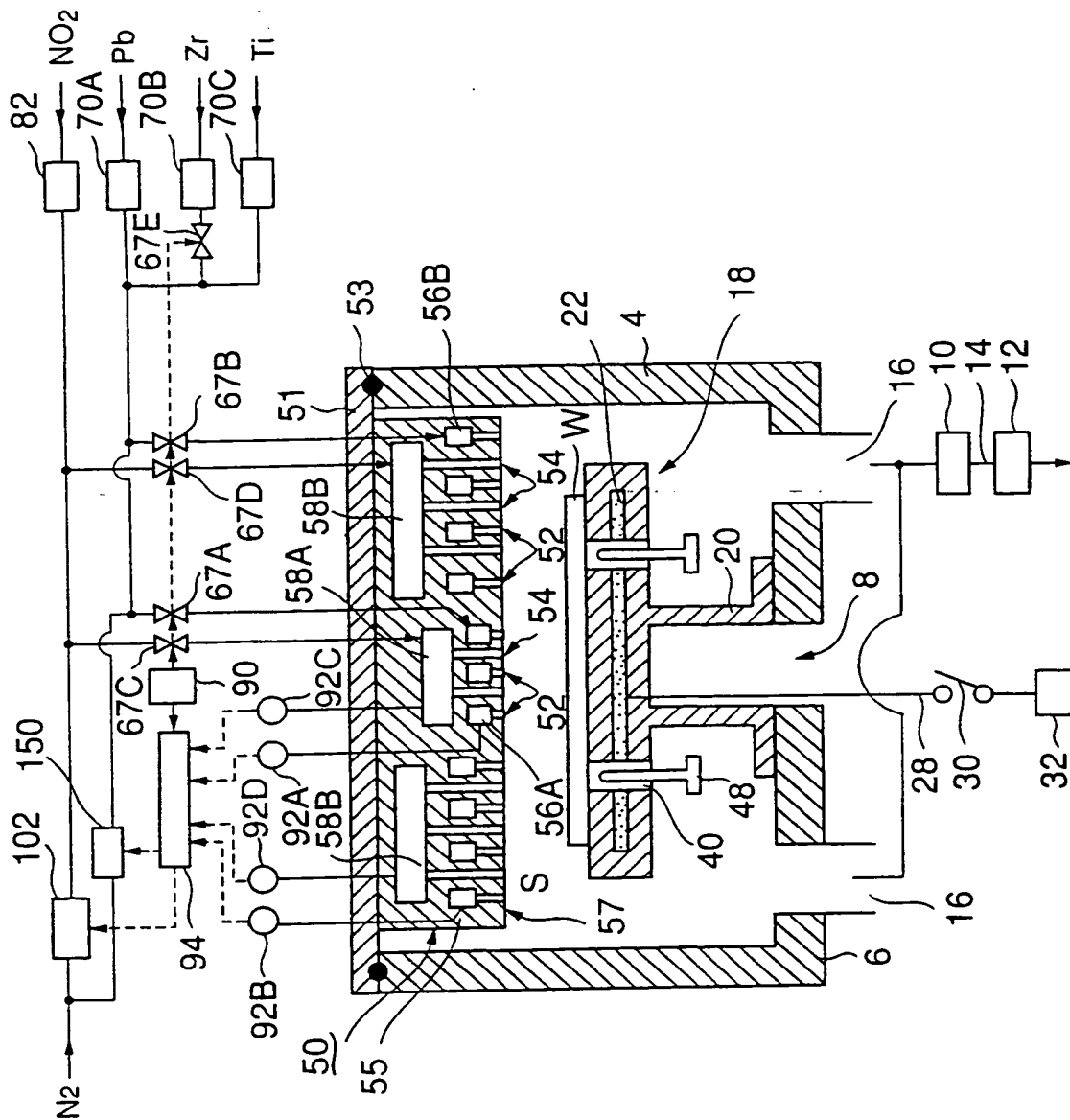


FIG.2

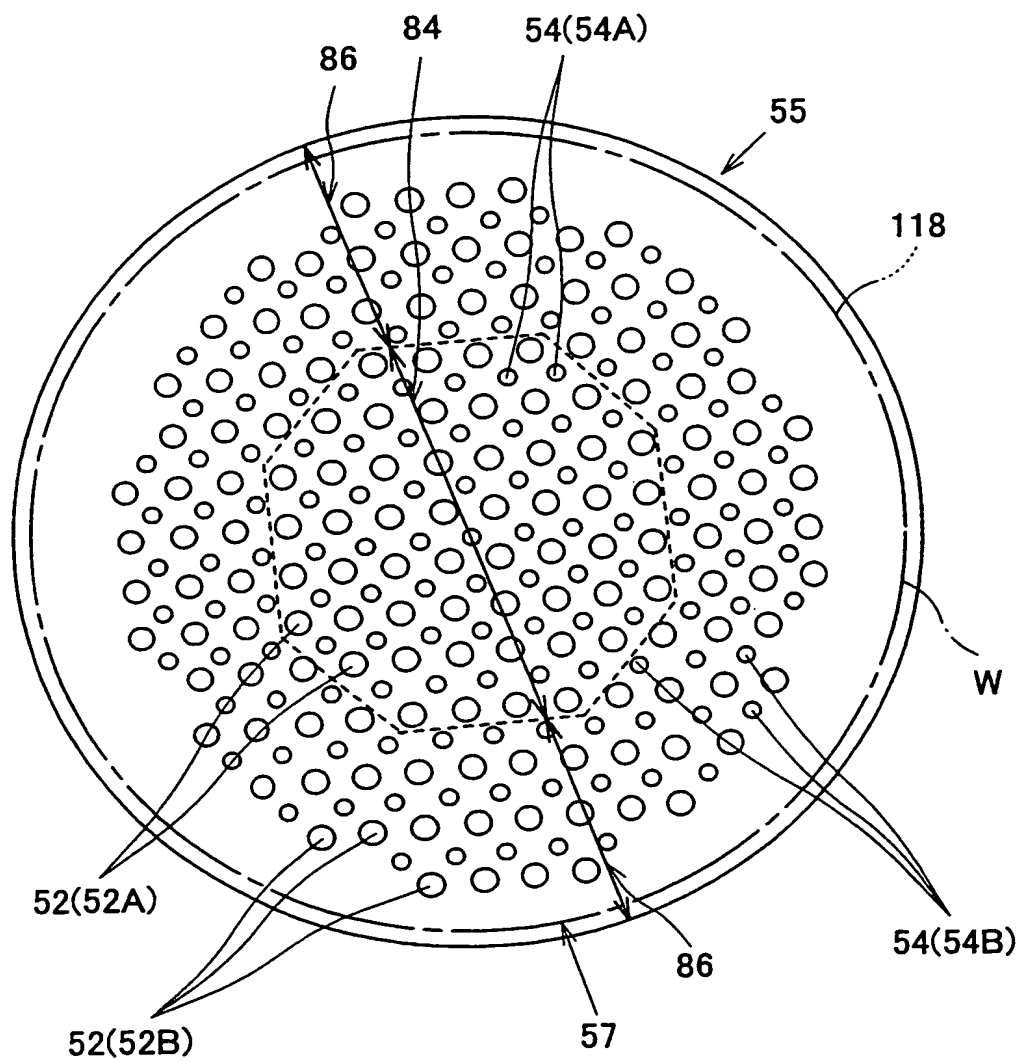


FIG. 3

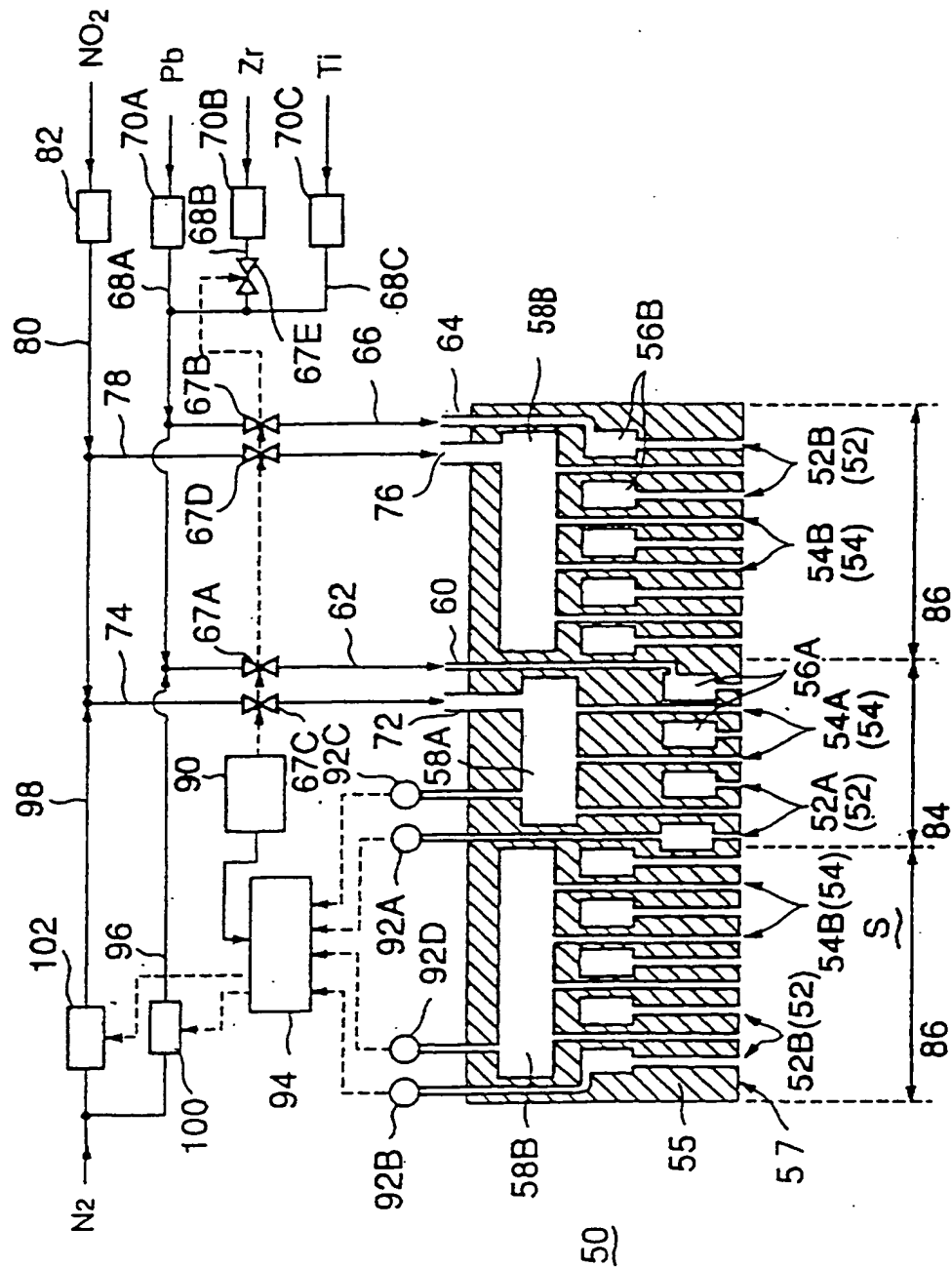


FIG. 4A

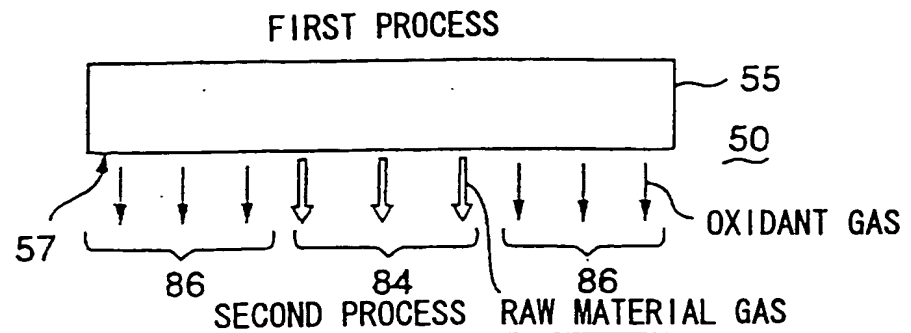


FIG. 4B

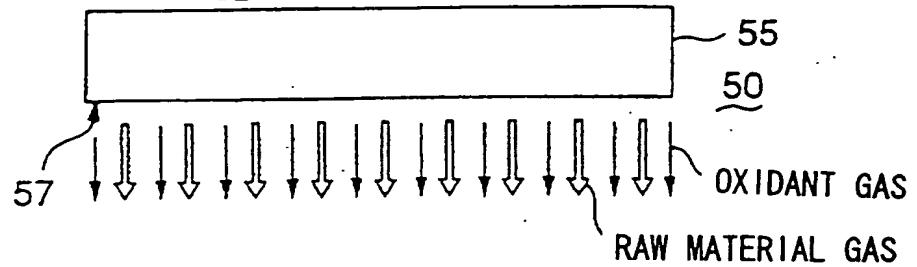


FIG. 5

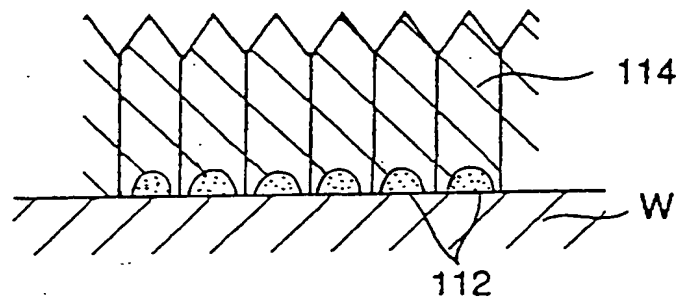


FIG. 6

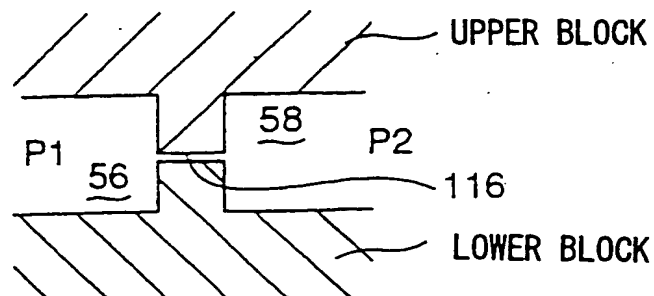


FIG. 7

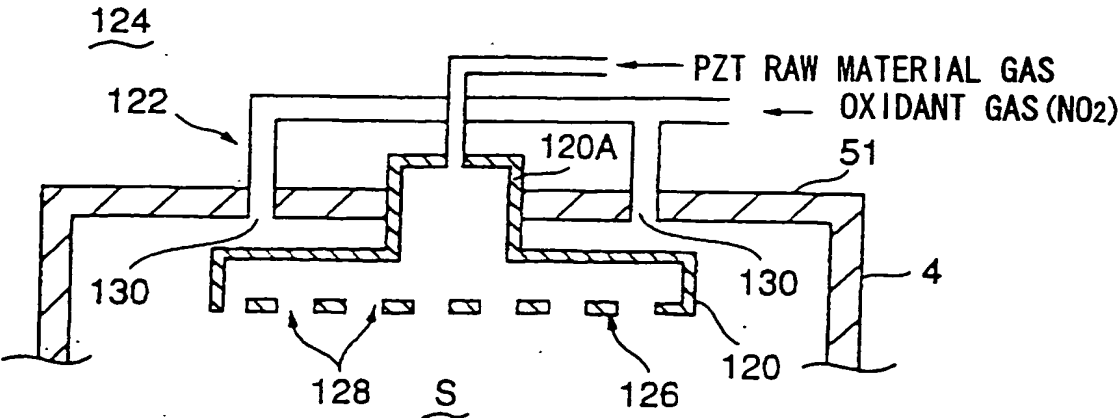


FIG. 8

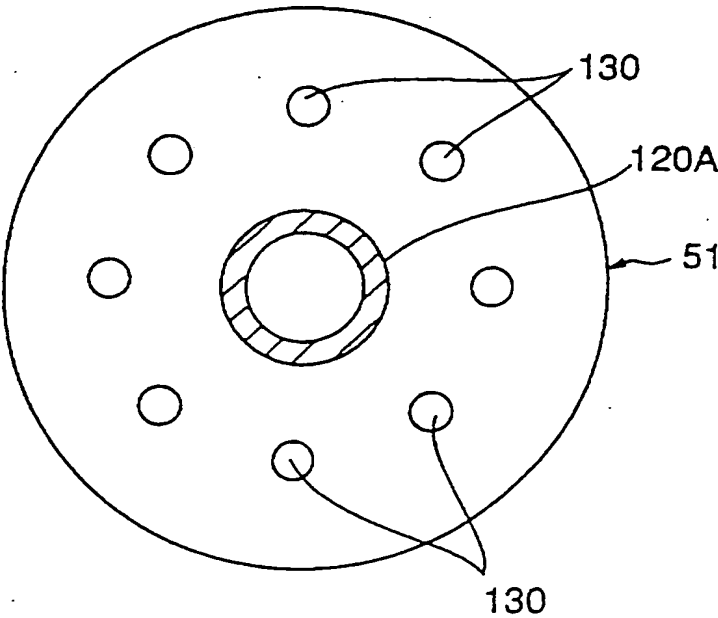


FIG. 9

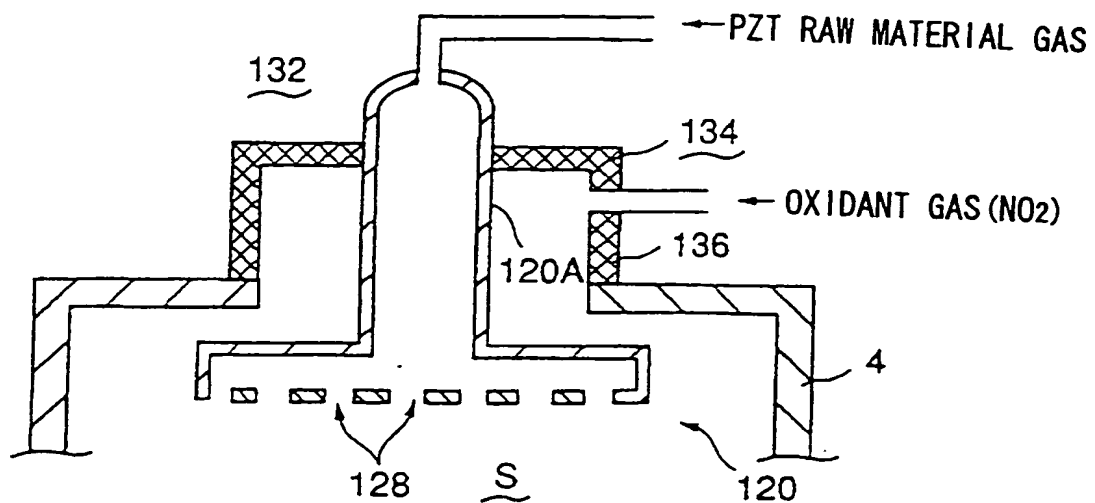


FIG. 10

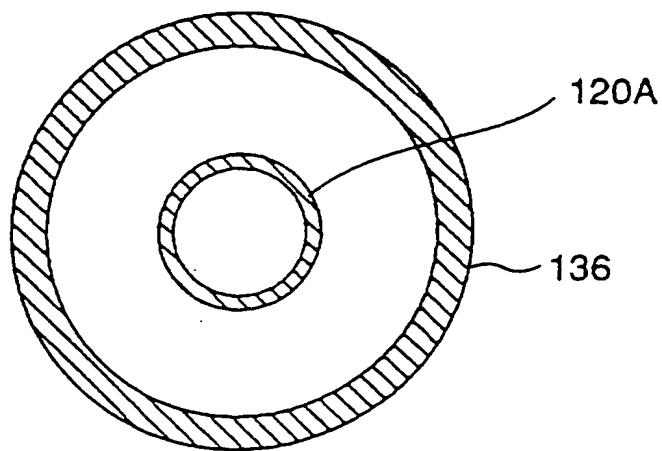


FIG. 11

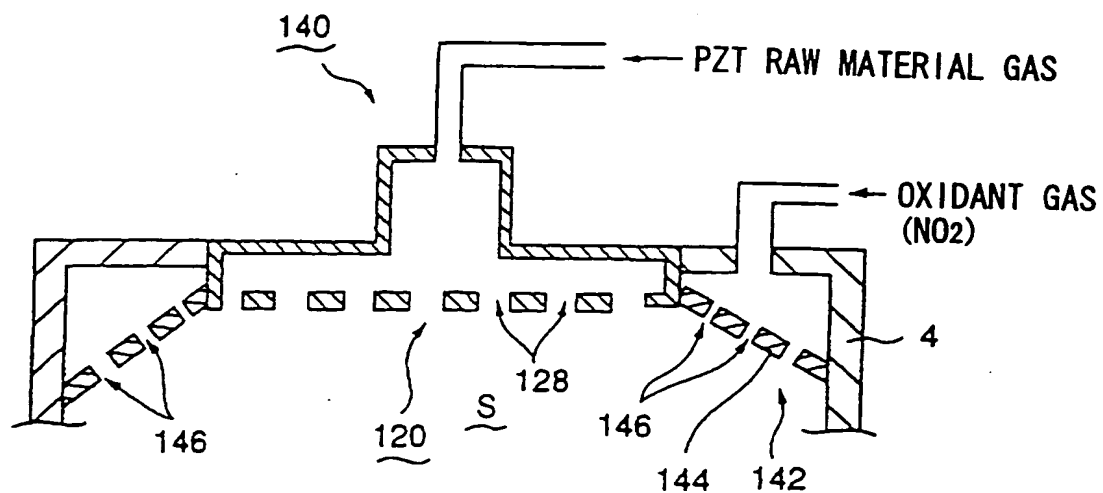


FIG. 12

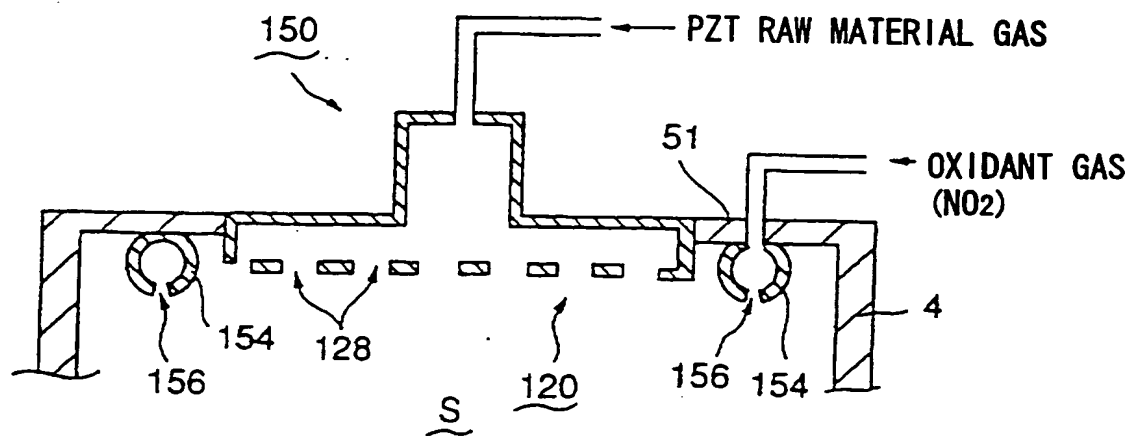
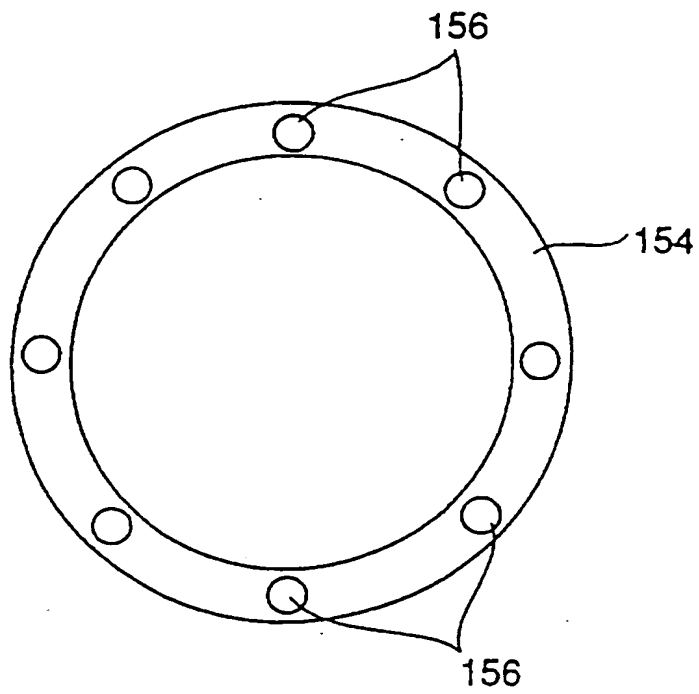


FIG. 13



INTERNATIONAL SEARCH REPORT

International Application No

PCT/JP 00/05858

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C23C16/455

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 821 084 A (APPLIED MATERIALS INC) 28 January 1998 (1998-01-28) column 8, line 22 -column 9, line 1 ----	1-14
A	PATENT ABSTRACTS OF JAPAN vol. 017, no. 538 (E-1440), 28 September 1993 (1993-09-28) & JP 05 152208 A (FUJITSU LTD), 18 June 1993 (1993-06-18) abstract ----	1-14
A	PATENT ABSTRACTS OF JAPAN vol. 010, no. 141 (E-406), 24 May 1986 (1986-05-24) & JP 61 005515 A (FUJITSU KK), 11 January 1986 (1986-01-11) abstract ----- -/-	1-14

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

28 November 2000

Date of mailing of the international search report

04/12/2000

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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

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US 5976261 A	02-11-1999	NONE	